Continuity Conditions for the Radial Distribution Function of Square-Well Fluids

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The continuity properties of the radial distribution function $g(r)$ and its close relative the cavity function $y(r) \equiv e^{\phi(r)/k_BT} g(r)$ are studied in the context of the Percus-Yevick (PY) integral equation for 3D square-well fluids. The cases corresponding to a well width, $(\lambda-1)\sigma$, equal to a fraction of the diameter of the hard core, σ/m, with $m = 1, 2, 3$ have been considered. In these cases, it is proved that the function $y(r)$ and its first derivative are everywhere continuous but eventually the derivative of some order becomes discontinuous at the points $(n+1)\sigma/m$, $n = 0, 1, \ldots$. The order of continuity (the highest order derivative of $y(r)$ being continuous at a given point), κ_n, is found to be $\kappa_n \sim n$ in the first case ($m = 1$) and $\kappa_n \sim 2n$ in the other two cases ($m = 2, 3$), for $n \gg 1$. Moreover, derivatives of $y(r)$ up to third order are continuous at $r = \sigma$ and $r = \lambda\sigma$ for $\lambda = 3/2$ and $\lambda = 4/3$ but only the first derivative is continuous for $\lambda = 2$. This can be understood as a non-linear resonance effect.

KEY WORDS: Radial distribution function; cavity function; square-well fluid; Percus-Yevick integral equation

I. INTRODUCTION

Simple models have played an important role in the development of liquid state theory, both as approximations and as useful reference systems in perturbation schemes. The simplest model with a repulsive hard core and an attractive well is the square-well (SW) fluid. The SW interaction potential is

$$\phi(r) = \begin{cases} \infty, & r < \sigma \\ -\epsilon, & \sigma < r < \lambda\sigma \\ 0, & r > \lambda\sigma, \end{cases} \tag{1}$$

where σ is the diameter of the hard core, ϵ is the well depth, and $(\lambda-1)\sigma$ is the well width. The equilibrium properties of the fluid depend on the values of three dimensionless parameters: the fraction of volume occupied by the spheres $\eta = \pi\rho\sigma^3/6$ (ρ being the number density), the reduced temperature $T^* = k_BT/\epsilon$ (T being the temperature and k_B being the Boltzmann constant), and the width parameter λ. These properties can be derived from a more fundamental quantity, the so-called radial distribution function $g(r)$ [1,2]. The quantity $4\pi r^2 g(r)dr/V$ is the probability that the centers of two spherical atoms in the liquid are separated by a distance between r and $r + dr$, V being the volume of the system. In the absence of particle interactions (ideal gases) there is no structure in the fluid and $g(r) = 1$. This is also true for any realistic potential in the limit $r \to \infty$ as we must have $\phi(r) \to 0$ in that limit. It is also evident that the centers of two particles in the SW fluid cannot be nearer than σ due to the hard core, so $g(r) = 0$ for $r < \sigma$. Many closed integral equations have been proposed for this function (YBG, HNC, Percus-Yevick, ...), but the most popular is, perhaps, the Percus-Yevick (PY) equation. In the search for these approximations it has been found useful to define an auxiliary function, the direct correlation function $c(r)$, through the Ornstein-Zernike (OZ) relationship

$$h(|\mathbf{r}_2 - \mathbf{r}_1|) = c(|\mathbf{r}_2 - \mathbf{r}_1|) + \rho \int d^3\mathbf{r}_3 c(|\mathbf{r}_1 - \mathbf{r}_3|)h(|\mathbf{r}_3 - \mathbf{r}_2|) \tag{2}$$

where $h(r) = g(r) - 1$. In this equation and the following ones we are assuming that the interaction potential is spherically symmetric and the structure functions, consequently, depends only on the distance between the particle centers. The physical meaning of the direct correlation function is clear; it accounts only for the correlation effects arising from a direct interaction between the particles in the fluid. Nevertheless, the total correlation function, $h(r)$, comprises also the correlations propagated by intermediate particles. The direct correlation function is expressed in terms of the so-called bridge functionals, which constitute an infinite sum of diagrams [1]. Integral equations are obtained by closing the OZ relation with an approximation for $c(r)$ based upon a sum of some set of these diagrams. By choosing an appropiate set of diagrams, Percus and Yevick [3,4] showed that the direct correlation function is approximately given by

$$c(r) = g(r)\left[1 - e^{\phi(r)/k_BT}\right] \tag{3}$$

According to (3) the range of $c(r)$ is equal to that of the interaction potential $\phi(r)$ as $c(r)$ is zero in those regions where the interaction potential vanishes. The PY equation is given by the substitution of (3) into the OZ relation (2) and it takes the form [1]

$$y(|\mathbf{r}_2-\mathbf{r}_1|) = A + \rho \int d^3\mathbf{r}_3\, f(|\mathbf{r}_1-\mathbf{r}_3|)\,[1+f(|\mathbf{r}_3-\mathbf{r}_2|)]\, y(|\mathbf{r}_1-\mathbf{r}_3|) y(|\mathbf{r}_3-\mathbf{r}_2|) \tag{4}$$

where $y(r) \equiv e^{\phi(r)/k_BT} g(r)$ is the cavity function, $f(r) = e^{-\phi(r)/k_BT} - 1$ is the Mayer function and A is a constant defined as

$$A = 1 - \rho \int_0^\infty dr f(r) y(r) 4\pi r^2 \tag{5}$$

The PY equation is exactly solvable for the hard-sphere (HS) fluid [5] and the sticky-hard-sphere (SHS) fluid [6]. Both models can be considered as special cases of the more general SW interaction: the HS potential is recovered if we take the limit $\epsilon \to 0$ (i.e., $T^* \to \infty$) or $\lambda \to 1$; the SHS fluid is defined by taking the limits $\lambda \to 1$ and $\epsilon \to \infty$ (i.e., $T^* \to 0$) simultaneously, while keeping the parameter $\tau^{-1} = 12\left(1-\lambda^{-1}\right) e^{1/T^*}$ constant.
Nevertheless, neither the PY equation nor any other integral equation for fluids has ever been analytically solved for the SW interaction. In 1977, Sharma and Sharma [7] proposed a mean spherical approximation which provides an analytical expression for the structure factor but it is not consistent with the hard core exclusion constraint. By the same time, Nezbeda [8] proposed a polynomial approximate solution for $y(r)$ valid in the limit $\lambda - 1 \ll 1$. This solution was based on the continuity of the first and the second derivatives of $y(r)$ at $r = \sigma$. More recently, Yuste and Santos [9] derived a simple approximate expression for the Laplace transform of $rg(r)$ for the SW fluid. This derivation is based upon simple physical requirements (finiteness of the radial distribution function at $r = \sigma^+$ and finite isothermal compressibility) and the continuity of $y(r)$ at $r = \lambda$.
The aim of this paper is the analysis of the continuity properties of the function $y(r)$ satisfying the PY equation for the three-dimensional SW fluid. First, we must identify the points at the borders of the regions where $y(r)$ is an analytic function. For $\lambda = 2$ it is clear that these points are given by $r = \sigma, 2\sigma, \ldots$, as also happens for the HS potential [1]. The radial distribution function is then divided in analytic pieces $\psi_0(r)$, $\psi_1(r)$, ... and the PY equation (4) is written as a system of non-linear integral equations for them. In these equations the Heaviside step function that enters in Eq. (4) through the Mayer function no longer appears. The continuity properties are derived from this system. The cases $\lambda = 3/2$ and $\lambda = 4/3$ are more cumbersome as the intervals cited above are divided into two and three equal parts, respectively, and the number of equations is obviously larger. More general cases with $1 < \lambda < 4/3$ are increasingly more difficult to manage since the number of intervals becomes larger and larger as the well width, $\lambda - 1$, becomes smaller. We will not deal with those cases in this paper.
The paper is organized as follows. In Sec. II the PY equation is set in a form that fits better our purpose and the continuity of $y(r)$ and its first derivative for $r = \lambda\sigma$ is suggested from the simulation results of Henderson *et al.* [10]. The appropiate system of integral equations for the case $\lambda = 2$ is written in Sec. III; the general derivatives are then related with the derivatives of lower order and the continuity conditions are derived recursively. A similar procedure is used in Sec. IV for the cases $\lambda = 3/2$ and $\lambda = 4/3$. The conditions for the HS fluid are given in an Appendix. The paper ends with some remarks on the relevance of these conditions for the proposal of approximations.

II. DEFINITIONS AND BASIC EQUATIONS

In the applications of the PY equation to simple potentials is often useful to define a new structure function $\psi(r) = ry(r)$, which satisfies the same continuity conditions as $y(r)$. After the change of variables $t = |\mathbf{r}_2 - \mathbf{r}_1|/\sigma$, $x = |\mathbf{r}_1 - \mathbf{r}_3|/\sigma$ and $y = |\mathbf{r}_3 - \mathbf{r}_2|/\sigma$ one can easily check that Eq. (4) takes the form [1]

$$\psi(t) = At + 12\eta \int_0^\infty dx f(x)\psi(x) \int_{|t-x|}^{t+x} dy\,[1+f(y)]\,\psi(y) \tag{6}$$

where

$$A = 1 - 24\eta \int_0^\infty dx f(x) x \psi(x) \tag{7}$$

It is remarkable that this reduction is only possible in three dimensions (excepting the one-dimensional case, where no reduction is necessary) and that the same change of variables in two dimensions yields a significatively more

complex integral equation due to the lack of rotational simmetry around the vector $\mathbf{r}_2 - \mathbf{r}_1$. The Mayer function $f(x) = \exp[-\phi(x)/k_B T] - 1$ for the SW interaction (1) is given by

$$1 + f(x) = H(x-1)\left[1 + \alpha H(\lambda - x)\right] \tag{8}$$

where $H(x)$ is the Heaviside step function and $\alpha \equiv \exp(\epsilon/k_B T) - 1$. The first derivative of $\psi(t)$ obtained from (6) is also given here for future reference

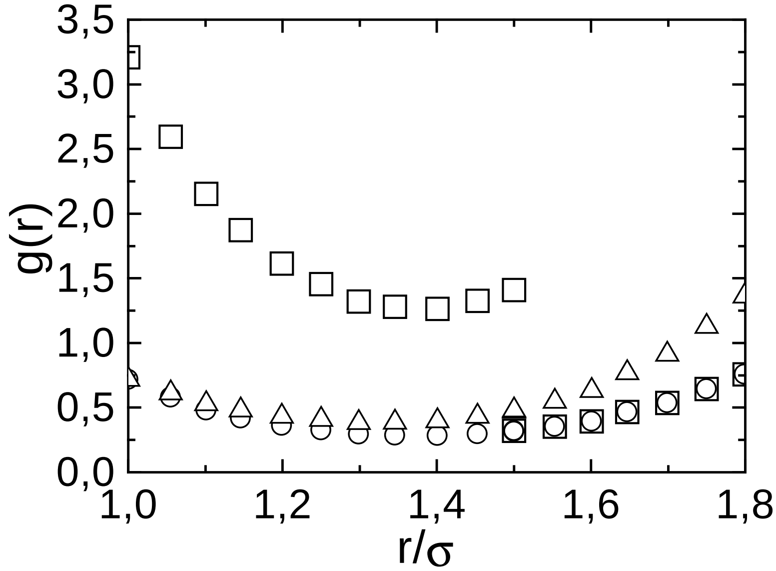

FIG. 1. Monte Carlo simulation results [10] for the structure functions $g(r)$ (squares), $y(r)$ (circles), and $\psi(r)$ (triangles) on a SW fluid with $\lambda = 3/2$, $T^* = 2/3$ and $\eta = 2\pi/15$. Note that $g(r)$ and $y(r)$ overlap for $r > \lambda\sigma$.

$$\begin{aligned} \psi'(t) &= A + 12\eta \int_0^\infty dx f(x)\psi(x)\left[1 + f(x+t)\right]\psi(x+t) \\ &\quad -12\eta \int_0^t dx f(x)\psi(x)\left[1 + f(t-x)\right]\psi(t-x) \\ &\quad +12\eta \int_t^\infty dx f(x)\psi(x)\left[1 + f(x-t)\right]\psi(x-t) \end{aligned} \tag{9}$$

In Fig. 1 the simulation results of Henderson *et al.* [10] for $g(r)$, $y(r)$ and $\psi(r)$ for a SW fluid with $\lambda = 3/2$, $T^* = 2/3$ and $\eta = 2\pi/15$ are shown. The radial distribution function is not continuous at $r = \lambda\sigma$ but both $y(r)$ and $\psi(r)$ are clearly continuous functions at that point. Simulation results also suggest the continuity of the first derivative but nothing can be said about the second or higher order derivatives as these are very difficult to measure in a simulation, where only results for widely spaced values of r are provided.

III. THE SQUARE-WELL FLUID WITH $\lambda = 2$

In this case the well width coincides with the diameter of the hard core and the function $\psi(t)$ that satisfies the corresponding PY equation (6) is conveniently defined in a piecewise fashion as follows

$$\psi(t) = \begin{cases} \psi_0(r) & 0 < r < 1 \\ \psi_1(r) & 1 < r < 2 \\ \vdots & \vdots \\ \psi_n(r) & n < r < n+1 \\ \vdots & \vdots \end{cases} \tag{10}$$

where we assume, to be confirmed later, that $\psi_n(r)$, $n = 0, 1, \dots$ are analytic functions in their intervals of definition. This will be justified by expressing (9) as a system of integral equations for these functions where the Heaviside step function in (8) no longer appears. Thus, any derivative of $\psi_n(r)$, $n = 0, 1, \dots$ is related to derivatives of lower order of the same set of functions. It can be expected that at a given point $t = n+1$, $n = 0, 1, \dots$ the functions $\psi_n(r)$ and $\psi_{n+1}(r)$ do not match perfectly and this gives rise to a difference between the derivatives of some order of these functions evaluated at that point. We define the symbols

$$\Delta_n^{(k)} = \psi_n^{(k)}(n+1) - \psi_{n+1}^{(k)}(n+1) \quad n = 0, 1, \dots, \quad k = 0, 1, \dots \tag{11}$$

as the jump in the derivative of order k evaluated at $t = n+1$. The continuity of $\psi(t)$ is a well known fact [8,9], so that we have $\Delta_n^{(0)} = 0$, $n = 0, 1, \dots$. The first derivative is given in (9) in terms of integrals over the functions $\psi(t)$ and $f(t)$, which in turn depends on the Heaviside step function. Starting from (9) and (8) the following set of equations for $\psi_n^{'}(t)$, $n = 0, 1, \dots$ is found

$$\begin{aligned}
\psi_0^{'}(t) = {} & A - 12\eta(\alpha+1) \int_{1-t}^{1} dx \psi_0(x)\psi_1(x+t) \\
& +12\eta\alpha(\alpha+1) \left\{ \int_{1+t}^{2} dx \psi_1(x)\psi_1(x-t) + \int_{1}^{2-t} dx \psi_1(x)\psi_1(x+t) \right\} \\
& +12\eta\alpha \int_{2-t}^{2} dx \psi_1(x)\psi_2(x+t)
\end{aligned} \tag{12}$$

$$\begin{aligned}
\psi_1^{'}(t) = {} & A - 12\eta \left\{ \int_{0}^{2-t} dx \psi_0(x)\psi_1(x+t) \right. \\
& \left. + \int_{2-t}^{1} dx \psi_0(x)\psi_2(x+t) - \int_{0}^{t-1} dx \psi_0(x)\psi_1(t-x) \right\} \\
& +12\eta\alpha \left\{ \int_{1}^{3-t} dx \psi_1(x)\psi_2(x+t) + \int_{3-t}^{2} dx \psi_1(x)\psi_3(x+t) \right. \\
& \left. - \int_{0}^{2-t} dx \psi_0(x)\psi_1(x+t) + \int_{0}^{t-1} dx \psi_0(x)\psi_1(t-x) \right\}
\end{aligned} \tag{13}$$

$$\begin{aligned}
\psi_2^{'}(t) = {} & A - 12\eta \left\{ \int_{0}^{3-t} dx \psi_0(x)\psi_2(x+t) + \int_{3-t}^{1} dx \psi_0(x)\psi_3(x+t) \right. \\
& \left. - \int_{0}^{t-2} dx \psi_0(x)\psi_2(t-x) - \int_{t-2}^{1} dx \psi_0(x)\psi_1(t-x) \right\} \\
& +12\eta\alpha \left\{ \int_{1}^{4-t} dx \psi_1(x)\psi_3(x+t) + \int_{4-t}^{2} dx \psi_1(x)\psi_4(x+t) \right. \\
& \left. - \int_{1}^{t-1} dx \psi_1(x)\psi_1(t-x) + \int_{t-2}^{1} dx \psi_0(x)\psi_1(t-x) \right\} \\
& -12\eta\alpha^2 \int_{1}^{t-1} dx \psi_1(x)\psi_1(t-x)
\end{aligned} \tag{14}$$

$$\begin{aligned}
\psi_n^{'}(t) = {} & A - 12\eta \left\{ \int_{0}^{n+1-t} dx \psi_0(x)\psi_n(x+t) + \int_{n+1-t}^{1} dx \psi_0(x)\psi_{n+1}(x+t) \right. \\
& \left. - \int_{0}^{t-n} dx \psi_0(x)\psi_n(t-x) - \int_{t-n}^{1} dx \psi_0(x)\psi_{n-1}(t-x) \right\} \\
& +12\eta\alpha \left\{ \int_{1}^{n+2-t} dx \psi_1(x)\psi_{n+1}(x+t) + \int_{n+2-t}^{2} dx \psi_1(x)\psi_{n+2}(x+t) \right.
\end{aligned}$$

$$
-\int_1^{t-n+1} dx\psi_1(x)\psi_{n-1}(t-x) - \int_{t-n+1}^2 dx\psi_1(x)\psi_{n-2}(t-x)\Big\}
$$

$$
-12\eta\alpha^2\int_{t-2}^2 dx\psi_1(x)\psi_1(t-x)\delta_{n,3}\,, \quad n\geq 3 \tag{15}
$$

With the PY equation written in the form of this system it is easy to show that $\Delta_n^{(1)}=0$, $n=0,1,\ldots$ as a consequence of the cancelation of some of the integral terms at the border points. The continuity of $\psi(t)$ and its first derivative is also true in the cases $\lambda=3/2$, $\lambda=4/3$, and in the HS fluid and it is possibly a general property of the PY equation. The derivatives of order k, $k\geq 2$ of $\psi_1(t)$, $\psi_2(t)$, etc...are obtained from the system of equations (12)–(15), yielding

$$
\psi_0^{(k)}(t) = -12\eta\sum_{j=0}^{k-2}(-1)^j\Big\{(\alpha+1)\psi_0^{(j)}(1-t)\psi_1^{(k-2-j)}(1)+\alpha(\alpha+1)\psi_1^{(k-2-j)}(1+t)\psi_1^{(j)}(1)
$$

$$
+\alpha(\alpha+1)\psi_1^{(j)}(2-t)\psi_1^{(k-2-j)}(2)-\alpha\psi_1^{(j)}(2-t)\psi_2^{(k-2-j)}(2)\Big\}+[\mathrm{Int}]\ , \tag{16}
$$

$$
\psi_1^{(k)}(t) = 12\eta\sum_{j=0}^{k-2}(-1)^j\Big\{\psi_0^{(j)}(2-t)\Delta_1^{(k-2-j)}+(1+\alpha)(-1)^j\psi_0^{(j)}(t-1)\psi_1^{(k-2-j)}(1)
$$

$$
-\alpha\psi_1^{(j)}(3-t)\Delta_2^{(k-2-j)}+\alpha\psi_0^{(j)}(2-t)\psi_1^{(k-2-j)}(2)\Big\}+[\mathrm{Int}] \tag{17}
$$

$$
\psi_2^{(k)}(t) = 12\eta\sum_{j=0}^{k-2}\Big\{(-1)^j\psi_0^{(j)}(3-t)\Delta_2^{(k-2-j)}-\psi_0^{(j)}(t-2)\Delta_1^{(k-2-j)}-\alpha(-1)^j\psi_1^{(j)}(4-t)\Delta_3^{(k-2-j)}
$$

$$
-\alpha\psi_0^{(j)}(t-2)\psi_1^{(k-2-j)}(2)-\alpha(\alpha+1)\psi_1^{(j)}(t-1)\psi_1^{(k-2-j)}(1)\Big\}+[\mathrm{Int}] \tag{18}
$$

$$
\psi_n^{(k)}(t) = 12\eta\sum_{j=0}^{k-2}\Big\{(-1)^j\psi_0^{(j)}(n+1-t)\Delta_n^{(k-2-j)}-\psi_0^{(j)}(t-n)\Delta_{n-1}^{(k-2-j)}
$$

$$
-\alpha(-1)^j\psi_1^{(j)}(n+2-t)\Delta_{n+1}^{(k-2-j)}+\alpha\psi_1^{(j)}(t+1-n)\Delta_{n-2}^{(k-2-j)}\Big\}
$$

$$
+12\eta\alpha^2\delta_{n,3}\sum_{j=0}^{k-2}\psi_1^{(j)}(t-2)\psi_1^{(k-2-j)}(2)+[\mathrm{Int}]\ , \quad n\geq 3 \tag{19}
$$

where the terms denoted by [Int] include the sum of several integrals over the functions $\psi_n(t)$, $n=0,1,\ldots$ and their derivatives. These terms are always continuous and their explicit expressions are not required for the calculation of the derivative jumps, so they will not be quoted here. If we take into account the continuity of $\psi(t)$ and its first derivative, as well as the condition $\psi(0)=0$, the first nonzero derivative jump at the border points $t=1,2,\ldots$ is readily derived from Eqs. (16)–(19):

$$
\Delta_0^{(2)} = \Delta_2^{(2)} = -24\eta\alpha(\alpha+1)\psi(1)\psi(2) \tag{20}
$$

$$
\Delta_1^{(2)} = 12\eta(\alpha+1)^2\left[\psi(1)\right]^2 \tag{21}
$$

$$
\Delta_3^{(2)} = 12\eta\alpha^2\left[\psi(2)\right]^2 \tag{22}
$$

$$
\Delta_{2n}^{(2n)} = -12\eta(\alpha+1)\psi(1)\Delta_{2n-1}^{(2n-2)}+12\eta\alpha\psi(2)\Delta_{2n-2}^{(2n-2)}\ , \quad n=2,3,\ldots \tag{23}
$$

$$
\Delta_{2n+1}^{(2n)} = 12\eta\alpha\psi(2)\Delta_{2n-1}^{(2n-2)}\ , \quad n=2,3,\ldots \tag{24}
$$

Therefore, the order of continuity (i.e., the highest order derivative of $\psi(r)$ being continuous) is $\kappa_n=1$ for $n\leq 3$, $\kappa_n=n-1$ for $n=4,6,\ldots$, and $\kappa_n=n-2$ for $n=5,7,\ldots$. The presence of discontinuities in the potential at $r=\sigma$ and $r=2\sigma$ gives rise to discontinuities in the second derivative of the structure function $\psi(r)$ not only at those points but also at their neighbors $r=3\sigma,4\sigma$ and, surprisingly, these discontinuities are of the same order as those at the hard core and square-well borders. At larger distances the structure function becomes more and more continuous and the order of continuity grows linearly. The derivative jumps in (23) and (24) may, indeed, increase exponentially

at certain physical conditions but this is balanced with the factorial in a Taylor expansion. These results are then compatible with the asymptotic limit $g(r) = y(r) \to 1$, or equivalently $\psi(r) \to r$, as $r \to \infty$. It can also be noticed that the first nonzero derivative jump in Eqs. (20)–(24) depends only on the packing fraction η, the temperature (through α), and the values of the function $\psi(r)$ at the potential discontinuity points. The order of continuity of the function $\psi(r)$ and the cavity function coincide by definition. The derivative jumps of the second derivative of $y(r)$ at $r = \sigma$ and $r = 2\sigma$ are given by

$$\left.\frac{d^2y}{dr^2}\right|_{r=\sigma^+} - \left.\frac{d^2y}{dr^2}\right|_{r=\sigma^-} = \frac{48\eta}{\sigma^2}\alpha(\alpha+1)y(\sigma)y(2\sigma) \tag{25}$$

$$\left.\frac{d^2y}{dr^2}\right|_{r=2\sigma^+} - \left.\frac{d^2y}{dr^2}\right|_{r=2\sigma^-} = -\frac{6\eta}{\sigma^2}(\alpha+1)^2\left[y(\sigma)\right]^2 \tag{26}$$

which are a consequence of Eqs. (20) and (21).

IV. THE SQUARE-WELL FLUIDS WITH $\lambda = 3/2$ AND $\lambda = 4/3$

In the case $\lambda = 3/2$ the function $\psi(t)$ is also piecewise but we must distinguish between the left and the right halves of the intervals $n < t < n+1$, $n = 0, 1, \ldots$:

$$\psi(t) = \begin{cases} \psi_0(t) & 0 < t < \frac{1}{2} \\ \overline{\psi}_0(t) & \frac{1}{2} < t < 1 \\ \vdots & \vdots \\ \psi_n(t) & n < t < n+\frac{1}{2} \\ \overline{\psi}_n(t) & n+\frac{1}{2} < t < n+1 \\ \vdots & \vdots \end{cases} \tag{27}$$

Consequently, the derivative jumps at the points $t = n + 1/2$ and $t = n + 1$, $n = 0, 1, 2, \ldots$ are denoted by two sets of symbols, $\widetilde{\Delta}_n^{(k)}$ and $\Delta_n^{(k)}$, respectively. These symbols are defined as follows

$$\widetilde{\Delta}_n^{(k)} = \psi_n^{(k)}(n+\frac{1}{2}) - \overline{\psi}_n^{(k)}(n+\frac{1}{2}) \tag{28}$$

$$\Delta_n^{(k)} = \overline{\psi}_n^{(k)}(n+1) - \psi_{n+1}^{(k)}(n+1) \tag{29}$$

As in the previous case the functions $\psi(t)$ and its first derivative are everywhere continuous and these symbols take the value zero for $k = 0$ and $k = 1$, $n = 0, 1, \ldots$. The equations for $\psi_n^{(k)}(t)$ and $\overline{\psi}_n^{(k)}$ are obtained from (8) and (9) after the elimination of the Heaviside functions. A straightforward but lengthy calculation that runs in parallel to that of Sec. III leads to the following results for the first nonzero symbols at every border point

$$\Delta_0^{(4)} = (12\eta)^2(1+\alpha)\psi(1)\left\{(1+\alpha)^2\left[\psi(1)\right]^2 + 2\alpha^2\left[\psi(3/2)\right]^2\right\} \tag{30}$$

$$\Delta_1^{(2)} = 12\eta(1+\alpha)^2\left[\psi(1)\right]^2 \tag{31}$$

$$\Delta_2^{(2)} = 12\eta\alpha^2\left[\psi(3/2)\right]^2 \tag{32}$$

$$\Delta_n^{(2n-2)} = -12\eta\left\{\psi(1)\Delta_{n-1}^{(2n-4)} - \alpha\psi(3/2)\widetilde{\Delta}_{n-1}^{(2n-4)}\right\}, \quad n \geq 3 \tag{33}$$

$$\widetilde{\Delta}_0^{(2)} = \widetilde{\Delta}_2^{(2)} = -24\eta\alpha(1+\alpha)\psi(1)\psi(3/2) \tag{34}$$

$$\widetilde{\Delta}_1^{(4)} = -(12\eta)^2\alpha\psi(3/2)\left\{\alpha^2\left[\psi(3/2)\right]^2 + 2(1+\alpha)^2\left[\psi(1)\right]^2\right\} \tag{35}$$

$$\widetilde{\Delta}_n^{(2n-2)} = -12\eta\left\{(1+\alpha)\psi(1)\widetilde{\Delta}_{n-1}^{(2n-4)} - \alpha\psi(3/2)\Delta_{n-1}^{(2n-4)}\right\}, \quad n \geq 3 \tag{36}$$

In this case we will denote the order of continuity at $t = n + 1$ by κ_n, $n = 0, 1, \ldots$ and the corresponding one at $t = n + 1/2$ by $\overline{\kappa}_n$, $n = 0, 1, \ldots$. According to (30)–(35) we conclude that $\kappa_0 = \overline{\kappa}_1 = 3$, $\kappa_1 = \kappa_2 = \overline{\kappa}_0 = \overline{\kappa}_2 = 1$,

and $\kappa_n = \overline{\kappa}_n = 2n-3$ for $n \geq 3$. It is a remarkable fact that the cavity function $y(r)$ is continuous up to the third order derivative at those points where the interaction potential exhibits discontinuities, $r=\sigma$ and $r=3\sigma/2$. Nevertheless, only the first derivative is continuous at the neighbour points $r=\sigma/2$, $r=2\sigma$, $r=5\sigma/2$ and $r=3\sigma$. The situation is rather different in the case studied in the previous Section. There, the discontinuity on the square-well is located precisely at a point where the hard core induces a discontinuity jump on the structure function. This special disposition of the potential jumps reinforces the discontinuity of the structure functions, $y(r)$ and $\psi(r)$, at the lattice sites $r/\sigma = 1, 2, \ldots$ on a kind of "resonance" effect. This is also observed at large distances from the hard core as the highest order derivative exhibiting no jumps grows as r in the SW fluid with $\lambda = 2$ and as $2r$ in the SW fluid with $\lambda = 3/2$, where the resonance condition is broken.

In the case $\lambda = 4/3$ we can find discontinuities at the points $t = n + 1/3$, $t = n + 2/3$, and $t = n + 1$, $n = 0, 1, 2, \ldots$. In a similar way to the definitions in (11), (28), and (29) the symbols $\widetilde{\Delta}_n^{(k)}$, $\widehat{\Delta}_n^{(k)}$ and $\Delta_n^{(k)}$ are introduced as follows

$$\widetilde{\Delta}_n^{(k)} = \lim_{\epsilon \to 0} \left[\left. \frac{d^k \psi(t)}{dt^k} \right|_{t=n+1/3-\epsilon} - \left. \frac{d^k \psi(t)}{dt^k} \right|_{t=n+1/3+\epsilon} \right] \tag{37}$$

$$\widehat{\Delta}_n^{(k)} = \lim_{\epsilon \to 0} \left[\left. \frac{d^k \psi(t)}{dt^k} \right|_{t=n+2/3-\epsilon} - \left. \frac{d^k \psi(t)}{dt^k} \right|_{t=n+2/3+\epsilon} \right] \tag{38}$$

$$\Delta_n^{(k)} = \lim_{\epsilon \to 0} \left[\left. \frac{d^k \psi(t)}{dt^k} \right|_{t=n+1-\epsilon} - \left. \frac{d^k \psi(t)}{dt^k} \right|_{t=n+1+\epsilon} \right] \tag{39}$$

where $n = 0, 1, \ldots$, $k = 0, 1, \ldots$. The calculation of these symbols is completely analogous to that of the previous cases save for the existence of three independent analytic functions on the intervals $(n, n+1)$, $n = 0, 1, \ldots$ and the details will not be given. The results for the nonzero symbols with the lowest value of k for $n = 0, 1, 2$ are

$$\widetilde{\Delta}_0^{(2)} = \widetilde{\Delta}_2^{(2)} = -24\eta\alpha(1+\alpha)\psi(1)\psi(4/3) \tag{40}$$

$$\widehat{\Delta}_0^{(4)} = -(12\eta)^2\alpha(1+\alpha)^2 \left[\psi(1)\right]^2 \psi(4/3) \tag{41}$$

$$\Delta_0^{(4)} = (12\eta)^2(1+\alpha)\psi(1) \left\{ (1+\alpha)^2 \left[\psi(1)\right]^2 + 2\alpha^2 \left[\psi(4/3)\right]^2 \right\} \tag{42}$$

$$\widetilde{\Delta}_1^{(4)} = -(12\eta)^2\alpha\psi(4/3) \left\{ \alpha^2 \left[\psi(4/3)\right]^2 + 2(1+\alpha)^2 \left[\psi(1)\right]^2 \right\} \tag{43}$$

$$\widehat{\Delta}_1^{(4)} = (12\eta)^2\alpha^2(1+\alpha)\psi(1) \left[\psi(4/3)\right]^2 \tag{44}$$

$$\Delta_1^{(2)} = 12\eta(1+\alpha)^2 \left[\psi(1)\right]^2 \tag{45}$$

$$\widehat{\Delta}_2^{(2)} = 12\eta\alpha^2 \left[\psi(4/3)\right]^2 \tag{46}$$

$$\Delta_2^{(4)} = -12\eta(1+\alpha)\Delta_1^{(2)} \tag{47}$$

Between these conditions and (30)–(36) corresponding to the case $\lambda = 3/2$ we notice some similarities. In particular, the order of continuity at the points $t = \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}$ and 3 for $\lambda = 3/2$ is the same that the order of continuity at the points $t = \frac{1}{3}, 1, \frac{4}{3}, 2, \frac{7}{3}$ and $\frac{8}{3}$ for $\lambda = 4/3$. Moreover, the first nonzero derivative jump has the same form in both cases if we write them in terms of $\psi(1)$ and $\psi(\lambda)$ (See Eqs. (34) and (40), (30) and (42), etc...). These considerations suffice us to conjecture that the order of continuity at the points $t = \lambda - 1, 2, \lambda + 1, 2\lambda$ is $k = 1$ and the order of continuity at $t = 1, \lambda$ is $k = 3$ for any value of λ in the interval $1 < \lambda < 2$. The special "resonant" case $\lambda = 2$ is excluded from this rule. The first nonzero derivative jumps at these points in terms of the cavity function are expected to be given by

$$\left. \frac{d^2 y}{dr^2} \right|_{(\lambda \pm 1)\sigma^+} - \left. \frac{d^2 y}{dr^2} \right|_{(\lambda \pm 1)\sigma^-} = \frac{24\eta\lambda}{(\lambda \pm 1)\sigma^2}\alpha(1+\alpha)y(\sigma)y(\lambda\sigma) \tag{48}$$

$$\left. \frac{d^4 y}{dr^4} \right|_{\sigma^+} - \left. \frac{d^4 y}{dr^4} \right|_{\sigma^-} = -\frac{(12\eta)^2}{\sigma^4}(1+\alpha)y(\sigma) \left\{ \left[(1+\alpha)y(\sigma)\right]^2 + 2\left[\alpha\lambda y(\lambda\sigma)\right]^2 \right\} \tag{49}$$

$$\left. \frac{d^4 y}{dr^4} \right|_{\lambda\sigma^+} - \left. \frac{d^4 y}{dr^4} \right|_{\lambda\sigma^-} = \frac{(12\eta)^2}{\sigma^4}\alpha y(\lambda\sigma) \left\{ \left[\alpha\lambda y(\lambda\sigma)\right]^2 + 2\left[(1+\alpha)y(\sigma)\ \right]^2 \right\} \tag{50}$$

$$\left.\frac{d^2y}{dr^2}\right|_{2\sigma^+} - \left.\frac{d^2y}{dr^2}\right|_{2\sigma^-} = -\frac{6\eta}{\sigma^2}\left[(1+\alpha)y(\sigma)\right]^2 \tag{51}$$

$$\left.\frac{d^2y}{dr^2}\right|_{2\lambda\sigma^+} - \left.\frac{d^2y}{dr^2}\right|_{2\lambda\sigma^-} = -\frac{6\eta\lambda}{\sigma^2}\left[\alpha y(\lambda\sigma)\right]^2 \tag{52}$$

which are a consequence of the generalization of (30)–(32), (34) and (35) or the corresponding conditions for $\lambda = 4/3$. Results for the order of continuity versus r/σ for the SW fluids we have analyzed and the hard-sphere case discussed in the Appendix are summarized in Fig. 2. The main feature of these series of values is their linear (HS) or staircase (SW with $\lambda = 2$, $3/2$ and $4/3$) behaviour beyond a given distance which depends upon the well width. This is a simple mathematical consequence of the explicit convolution nature of the PY equation. It can be shown that a solution of this kind of equations with order of continuity p at $r = a$ and $p^{'}$ at $r = b$ is necessarily a function with order of continuity $p + p^{'} + 3$ at $r = a + b$. This rule is sufficient to explain the trend for $r \geq 3\sigma$ on every case plotted in Fig. 2. Discontinuities of the structure functions derivatives appear at $r = \sigma$ and $r = \lambda\sigma$ as a consequence of the singularities of the interaction potential, $\phi(r)$, and are then propagated in a way we are not familiar with in the domain of linear physics. The cases analyzed in detail in this paper give us also some insight on the interplay of the relative positions of the discontinuites of the potential and we could suggest an explanation for the qualitatively different behaviours of the cases $1 < \lambda < 2$ and $\lambda = 2$ showed in Fig. 2. The order of continuity appears to be generally lower in the latter case and we can attribute that to an interference of the singularities of the Mayer function because for $\lambda = 2$ the square-well border is placed precisely on a point

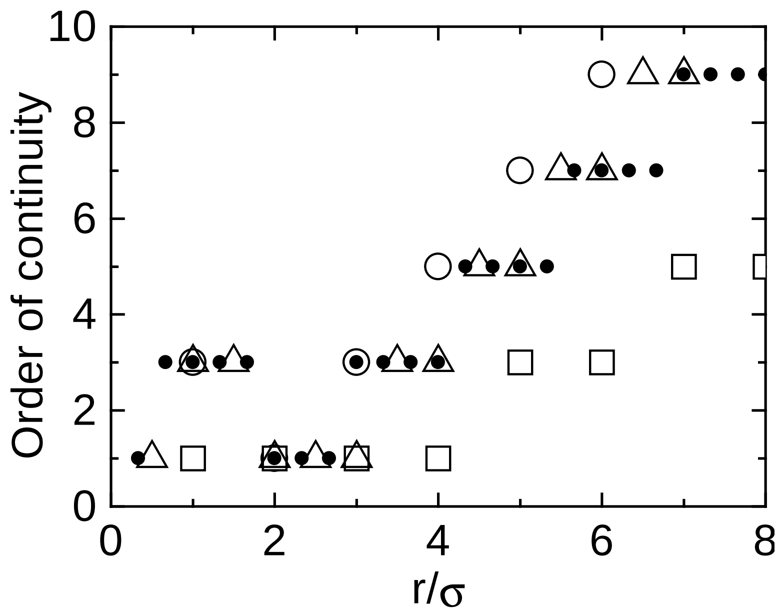

FIG. 2. Order of continuity of $y(r)$ versus r/σ for the SW fluid with $\lambda = 2$ (squares), $\lambda = 3/2$ (triangles), and $\lambda = 4/3$ (dots), and the HS fluid (circles). The order of continuity is assumed to be infinity if not plotted.

where the singularities induced by the hard core are propagated to. Conjectures about what will occur with arbitrary values of λ are discussed in the next section.

V. CONCLUDING REMARKS

In this paper the analytic properties of the structure function of square-well (SW) fluids have been studied. The SW potential is a simple but useful model of more realistic interactions as it includes not only the volume exclusion effect of the hard core but also a finite range attractive part. It has been used as a model for fluids, systems of colloidal particles, microemulsions and micelles [11–15]. Throughout this paper, it has been assumed that the structure function $\psi(r) = ry(r)$ satisfies the well known nonlinear Percus-Yevick (PY) integral equation. Despite the apparent simplicity of the SW potential, no exact solution of this equation has ever been found. The reduction of the PY equation to a system of nonlinear integral equations unveils the degree of difficulty of the problem. The structure function, $\psi(r)$, must be defined by analytical pieces and this is unsuitable for a purely local treatment, except in the hard-sphere [3]

and sticky-hard-sphere [6] models, where an expression for the Laplace transform of $rg(r)$ was found.
Although we have restricted ourselves to the cases $\lambda = 2$, $\lambda = 3/2$ and $\lambda = 4/3$, the general pattern for any value λ seems clear. If λ is an integer we have discontinuities only at $r/\sigma = 1, 2, \ldots$, the "resonance" condition is fulfilled and the order of continuity grows as r for large r. If λ is not an integer we must expect the appearance of discontinuities at those points which can be expressed as a linear combination of the fundamental scale lengths σ (the hard core diameter) and $(\lambda-1)\sigma$ (the SW width), $n\sigma + m(\lambda-1)\sigma$, where n and m are integers. If λ is a rational number there is some point that can be obtained by using two different pairs of integers (n, m) and the location of the discontinuity points repeats periodically after that. That is not the case for irrational values of λ. A direct consequence of the choice of a width well $(\lambda-1)\sigma$ incommensurate with the hard core diameter σ is that the order of continuity at $r/\sigma = 1, 2, \ldots$ will possibly coincide with the corresponding to the HS fluid because the two discontinuities of the interaction potential do not interfere in this case. In the cases we have discussed ($\lambda = 3/2$ and $\lambda = 4/3$) there is still some kind of "resonance" and this gives rise to an order of continuity lower in two units to that of the HS fluid at $r/\sigma = 4, 5 \ldots$ (See Fig. 2). However, the conjecture expressed in Eqs. (48)–(52) for $1 < \lambda < 2$ is sufficient for the purpose of the search of approximate structure functions as only this interval is considered physically meaningful in the applications of the model to simple fluids or colloids. We must also emphasize that these results have been derived in the context of the PY equation but, referring only to the key features of the structure functions, it is possible that they are more general. An analysis of other integral equations for fluids and the Mayer diagrams not taking into account by them would be necessary in order to clarify this point.
This work was already started in the early days of the theory of liquids. Percus showed [4], in the context of the PY equation for hard spheres, that analytic breakings on the structure functions should appear whenever distances between particle centers along a chain are modified so to accommodate a new particle. This result explains the discontinuites on the cavity function derivatives at $r = \sigma$, 2σ, 3σ, $\ldots$ that are listed in the Equations (A4)–(A5). A combination of formal and heuristic geometric arguments were used later by Stillinger [16] in order to identify the diagrams which cause discontinuities in the derivatives of $g(r)$ for hard spheres up to fourth order in the density. The most simple diagrams are the chains but we have also double chains and triply-connected diagrams that are not included in the PY approximation. The topological change associated with the separation or the approaching of a given pair of spheres in the cluster corresponding to the diagram within a distance which avoids the contact of all the particles was found to be the origin of a singularity of the structure function. In that way, the lowest-order double chain gives rise to a singularity at $r = \sqrt{3}\sigma$ and the lowest-order triply-connected cluster is responsible for a discontinuity at $r = \sqrt{8/3}\sigma$ [17]. Careful Monte Carlo simulations carried out by Seaton and Glandt [18] for the fluid of adhesive spheres have confirmed the existence of discontinuities of the radial distribution function at $r = \sqrt{8/3}\sigma$, $\sqrt{3}\sigma$ and 2σ. The latter is the most striking one and this is taking into account by the PY solution because it is originated by the chain diagram with two bonds. The more complex spatial diagrams are responsible for the discontinuities at $r = \sqrt{8/3}\sigma$ and $\sqrt{3}\sigma$ which are not included in the PY solution for the sticky hard sphere potential [6]. Nevertheless, these two are less prominent features of $g(r)$ than the discontinuity at $r = 2\sigma$ and the PY solution gives a good overall agreement with Monte Carlo simulation results [18]. Stillinger [16] has even suggested that the full set of singularities of $g(r)$ for the hard sphere or hard disk case is dense throughout the entire range $0 \le r < \infty$ as a consequence of the formation or breaking of bonds on random packings when r (the distance between two given particles in the cluster) is slightly varied.
Analytical approximations proposed by different routes are equally interesting alternatives to the solution of the integral equations. These approximations are usually based on the imposition of continuity conditions at the hard core and the SW border. For example, the approximation of Nezbeda [8] for a very thin SW interaction is based upon the continuity of the first and the second derivatives of $y(r)$ at $r = \sigma$. On the other hand, Yuste and Santos [9] proposed an approximation on the basis of some physical conditions, among which the continuity of $y(r)$ at $r = \lambda\sigma$. The latter authors are forced to fix one of the parameters of their model at its low density value in order to close the system of nonlinear equations that those parameters satisfy. The results derived in Secs. III and IV allow the imposition of continuity conditions on the first derivative of $y(r)$ at $r = \lambda$ and this would close the system of equations of Yuste and Santos's model in a more convincing way. Similarly, Nezbeda approximation could possibly be improved by imposing the continuity of the third derivative at $r = \sigma$. Work along this line is currently in progress and will be published elsewhere.

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APPENDIX A: THE HARD-SPHERE FLUID

In this case the structure function $\psi(t)$ is defined in the piecewise form given in (10) and the set of equations satisfied by the analytic functions $\psi_n(t)$, $n = 0, 1, \ldots$ is obtained from (12)–(15) if the limit $\alpha \to 0$ is taken (which is equivalent to take $\epsilon \to 0$ or $T \to \infty$). The derivatives of order k, $k \geq 2$ has already been given in Eqs. (16)–(19). By setting $\alpha = 0$ in these equations we get

$$\psi_0^{(k)}(t) = -12\eta \sum_{j=0}^{k-2} (-1)^j \psi_0^{(j)}(1-t)\psi_1^{(k-2-j)}(1) + [\mathrm{Int}] \tag{A1}$$

$$\psi_1^{(k)}(t) = 12\eta \sum_{j=0}^{k-2} \left\{ (-1)^j \psi_0^{(j)}(2-t)\Delta_1^{(k-2-j)} + \psi_0^{(j)}(t-1)\psi_1^{(k-2-j)}(1) \right\} + [\mathrm{Int}] \tag{A2}$$

$$\psi_n^{(k)}(t) = 12\eta \sum_{j=0}^{k-2} \left\{ (-1)^j \psi_0^{(j)}(n+1-t)\Delta_n^{(k-2-j)} - \psi_0^{(j)}(t-n)\Delta_{n-1}^{(k-2-j)} \right\} + [\mathrm{Int}] \;, \quad n \geq 2 \tag{A3}$$

where the terms [Int] again denote the sum of several integrals over the functions $\psi_0(t)$, $\psi_1(t)$, $\ldots$, whose explicit expressions are not required as these terms are always continuous at the points of interest $t = 1, 2, \ldots$. The derivative jumps $\Delta_n^{(k)}$, $n = 0, 1, \ldots$, $k = 0, 1, \ldots$ have been already defined in (11) and the nonzero symbols $\Delta_n^{(k)}$ corresponding to the lowest value of k for every n can be derived from (A1)–(A3). The results are

$$\Delta_0^{(4)} = -12\eta\psi_1(1)\Delta_1^{(2)} - 24\eta\psi_1(1)\psi_0^{(2)}(0) = (12\eta)^2 \left[\psi(1)\right]^3 \tag{A4}$$

$$\Delta_n^{(2n)} = (12\eta)^n \left[-\psi(1)\right]^{n+1} \;, \quad n \geq 1 \tag{A5}$$

where $\psi(1) = (1 + \eta/2)/(1-\eta)^2$ is the PY exact result [3] for the structure function at the hard core contact point. Note that the HS fluid can also be seen as a SW fluid in the limit $\lambda \to 1$.

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